

P1 1116428

RECEIVED

22 JAN 2004

WIPO

PCT

# THE UNITED STATES OF AMERICA

**TO ALL TO WHOM THESE PRESENTS SHALL COME:**

UNITED STATES DEPARTMENT OF COMMERCE  
United States Patent and Trademark Office

January 16, 2004

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.**

**APPLICATION NUMBER:** 60/425,236

**FILING DATE:** November 12, 2002

**RELATED PCT APPLICATION NUMBER:** PCT/US03/36101

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS



*M. Sias*  
M. SIAS  
Certifying Officer

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

11/12/02  
1135 U.S. PTO

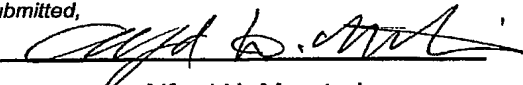
PTO/SB/16 (10-01)  
Approved for use through 10/31/2002. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE  
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
Andrew T.		HUNT		Atlanta, GA	
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
CARBONACEOUS MATERIALS					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number		24948		Place Customer Number Bar Code Label here	
OR					
<input type="checkbox"/> Firm or Individual Name					
Address					
Address					
City		State		ZIP	
Country		Telephone		Fax	
ENCLOSED APPLICATION PARTS (check: all that apply)					
<input checked="" type="checkbox"/>	Specification	Number of Pages	7	<input type="checkbox"/>	CD(s), Number
<input type="checkbox"/>	Drawing(s)	Number of Sheets		<input type="checkbox"/>	Other (specify)
<input type="checkbox"/>	Application Data Sheet. See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/>	Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)  \$80.00
<input type="checkbox"/>	A check or money order is enclosed to cover the filing fees				
<input checked="" type="checkbox"/>	The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 501231				
<input type="checkbox"/>	Payment by credit card. Form PTO-2038 is attached.				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,  
SIGNATURE   
TYPED or PRINTED NAME Alfred H. Muratori  
TELEPHONE (678) 287-2434

Date 11/05/2002  
REGISTRATION NO.  
(if appropriate)  
Docket Number:

41,561  
0175-PR

## USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

## CARBONACEOUS MATERIALS

### Field of the Invention

- 5        The present invention is directed to the formation of carbonaceous materials. In particular, the invention is directed to using a spray system to form carbonaceous materials.

### Background of the Invention

- 10        Spray systems are well known in the art, wherein carbon particles can be made by very fuel rich flame combustion systems or thermal cracking of hydrocarbon materials. These materials historically have been made from gas-based materials and sprayed materials. In the gas-based systems the hydrocarbon feed stock material is fed in as a gas and then partially burned or thermally cracked. After which, the soot is formed and collected. In the liquid spray systems,  
15        droplets of material are formed that are ten to hundreds of microns in size. These are then fed into a hot zone. The hot zone in most cases is a flame and the flame is produced via gaseous hydrocarbons mixed with oxygen containing gases, such as air, which enable high flow. This primary burn enables better atomization and cracking of the liquid feed stocks. The liquid feed stocks in most cases is oil.

### 20        Summary of the Invention

- The current invention is the utilization of ultra-fine droplets even sub-micron size droplets which prior to this invention have not been used in the art to form carbonaceous materials. Extremely fuel rich mixtures are formed creating an incomplete combustion environment or are fed into a thermal reactor where cracking of the hydrocarbon occurs. In both  
25        cases, an environment exists where freed carbon is produced which readily condensates forming very fine carbonaceous material in the form of soot.

      The issue with the current materials is that they can range in size and can be highly agglomerated such that the individual particles are difficult if not impossible to break up thus

0175-PR

creating an overall particle size much larger than that desired for many applications. For many of these agglomerates, the particles vary in size tremendously by several orders of magnitude. Even the primary particles making up the agglomerates can vary in size by a few x. It is, therefore, desired to produce more uniform and smaller sized soots and carbonaceous materials for a wide range of applications. To achieve this result in a manner that is low cost for large scale manufacturing processes is also of great desire.

A recent innovation, as described in US Patent Numbers 5,997,956 and 6,132,653, have enabled the formation of various compounds in nanoparticle form. This innovative technique is identified as a candidate process for enabling the desired forms of carbonaceous material to be formed. The key to forming the materials is that the combustion system, rather than having a primary gas flame to form the heat and environment for the vaporization and reaction of the oil or other carbon-based source material, uses a method wherein these materials are premixed. This premixing can be done either in a single container, through different feed lines and mixed in a smaller mixing chamber or fed into a single line in which it enables enough mixing to obtain the desired uniformity. The mixture or liquid is fed into the Nanospray<sup>SM</sup> system, that will create ultra-fine droplets of more uniform size and distribution along with gas products that can create a burn zone even from a single feedstock. While this single feedstock is desired, it should be noted that small amounts of gases for pilots to ensure the continued combustion due to the higher velocities to form smaller non-agglomerated particles can be used. The smaller size can be maintained without agglomeration by having a rapid quench after the flame sector. The quench will be brought about by the introduction of cooling mediums. Water has one of the highest heat absorption capabilities and therefore, is one of the lowest cost and one of the most efficient cooling mediums. Any liquid cooling medium, however, can be used including various gases, other liquids (such as liquid nitrogen) to bring about rapid quench of the formed carbonaceous materials which then are collected by any of the numerous different methods that exist in the art.

Solutions of interest include oils and can be combined with gases such as propane, natural gas, acetylene, butane, etc., or the primary carbon source could be other high carbon containing materials such as xylene or toluene. It is preferred to use an absorbed gas that is a ready producer

0175-PR

of carbon such as acetylene and other high carbon producing potential fluids with low boiling points. Non-flammable gasses, such as  $N_2$ , Ar and  $CO_2$  can also be dissolved into the liquid carbon source to aid atomization. Additions of oxidizers such as  $NO_2$  or  $O_2$  can result in explosive fluids and should be avoided unless fool-proof systems are used. Oxidizers can further  
5 reduce droplet evaporation, flame diffusion zones, but can be very dangerous if not mixed and handled properly with the fuels. Ideally these oxidizers are introduced near the atomizing device and the fluids are moving faster than the combustion/flame velocity so that the combustion front cannot propagate into the fluid system. Thus the fuel atomizing benefactor itself can be used to yield the product.

10 Pilots are desired to have a short reaction time, so continuous pilot(s) or a short primary burn zone is used to ensure the combustion of the materials. In close proximity to the point of introduction of the Nanospray<sup>SM</sup> the correct amount of oxidizer whether as air, a gas, or oxygen is introduced to create a primary burn or combustion zone such that the evolution of the freed carbon from hydrocarbon material can be accomplished. By having such a well mixed oxygen  
15 and carbon precursor spray in such fine atomization, the vaporization time is reduced and thus the reaction zone can be minimized thereby reducing the time of exposure to the reaction to less than 10 milliseconds, even more desirably less than 5 milliseconds, and even more desirably in the 0.1-2 millisecond time range.

In the high heat zone for the cracking and evolution of free carbon from which the soot  
20 can form, it is also desired to rapidly quench the material so that the carbon soots primary particles do not form larger hard agglomerates. Therefore, the cooling medium would be fed very proximal to the end of the burn zone. The better the mixing of the cooling medium with the material, the more rapid the cooling can occur. Currently large coolant droplets are sprayed into the hot residual gases and soot, in which local cool zones near the water droplets occur. It is  
25 preferred to have a more homogenous dense spray, so the quenching is more uniform. Causing a more uniform and more rapid cool, results in producing more uniform and finer carbonaceous materials. The material produced can be just carbon or primarily carbon. The feed stocks can also contain precursors of materials that can modify the carbon. Materials that can be fed in and

0175-PR

dissolved into the primary systems or can be fed into separate nearby flames, that would feed in material, thus forming materials on which the carbon can nucleate and grow. Alternatively, precursor materials to coat the carbon after it is formed can be fed in close proximity or downstream of the carbon condensation.

5        So with toluene, xylene, or even an oil-based solution, a wide range of precursors, as disclosed in U.S. Patent Numbers 5,652,021, 5,858,465, 5,863,604, 6,013,318, 6,368,665 and the previously cited patents, can form materials as a primary nucleator for the growth of carbonaceous material or can be inter-dispersed within the carbon-formed material. If it is desired to have a more highly conductive carbon, then materials such as nickel, copper and other  
10        conductive metals can be formed with the carbon. It may also be desired to have some elements contained with the carbon such that a top coated material on the carbon will be more stable. Such top coating materials can be catalysts for applications such as refining chemical processing and fuel cells. Materials that may enable the further stability, lower surface energy absorption of catalysts include ceria, lanthanum, nickel and other materials. When platinum or other catalysts  
15        are further deposited, from gas streams, onto the virgin, simultaneously formed carbon, they can remain more stable over time yielding net effective higher surface areas over prolonged usages. By forming on virgin surfaces at elevated temperatures, the catalysts or other co-formed materials minimize interfacial energy which yields increased adhesion and stability.

      In many cases, it is desired to have a very uniform mixture of both carbon, carbon black  
20        and carbonaceous material along with additional materials such as for batteries, catalysts and other applications. In these cases, flames can be made wherein in one flame the metal containing complex materials can be made and in other flames, the carbonaceous material can be formed. By co-producing these materials, a more uniform and homogenous mixture prior to agglomerations of either set of particles can occur. An important aspect of the current invention  
25        is that separate flames can contain different materials or separate reaction zones of thermal energy can contain the right properties for reaction. Materials can be made wherein the net resulting product flowing in a continuous gas stream is particles of carbonaceous material being intermixed with another predominately non-carbonaceous material, such that metals, oxides,

0175-PR

polymers are all formed or combinations thereof are formed with particles that are primarily carbonaceous.

By doing this in a single step, one of the great issues is overcome wherein the mixing of materials that are currently formed by separate processes and an agglomeration occurs prior to coating the carbon. These aggregates of small particles can be so tightly bound that they cannot be broken up and the desired fully uniform mixing is extremely difficult if not impossible to achieve. The current invention simplifies this, reduces the number of steps and yields a better more uniform mixture of desired small particles and nanoparticles of material.

The sequence in the feeding of the different materials to get uniform mixtures can be important. This is particularly important, if certain materials enable the seeding of certain growth phases of other materials such that the primary material is formed prior to the formation of the second. Such as in the growth of more expensive or desired phases like crystalline materials like platinum that have a similar structure so that the platinum has the right form but less platinum is needed to result in crystalline growth. Alternatively, there are catalyst or seeds for growing certain phases of carbon such as graphite or fullerenes  $C_{60}$  (also known as buckminsterfullerene which can be formed as "buckyballs" or tubes) type structures. It is thus desired to have the seed or nucleus material form prior to the second material. In the case of fullerene type materials, there are a number of well known materials that can be used to grow nanotubes and other structures or even a graphite sheet if desired for needed structures. Once again the agglomeration issue is minimized by instead forming the core material in situ. Uniformly and better distributed unagglomerated seed stock is produced.

Small primary flames thus could be made which contain the precursors to form the desired starting materials and these primary flames can act as the preburn initiator for the formation of the carbonaceous materials which could be sprayed in these primary flames which then act as a pilot to sustain the combustion. There maybe sub-pilots for these primary particle producing flames which then would be an array of flames centered in an array of sprays of the main carbon precursor materials which could be sprays or gases of carbon source materials. Alternatively if a combustion process is not used to form the carbon, a wide range of other

0175-PR

processes to form the carbon can be made including evaporation of carbon and all other known forms of carbon. Heterogeneously formed carbon structures can then be seeded off of the primary particle materials. It is known that such materials as iron, nickel, cobalt, and alloys thereof with a wide range of other materials can be used for seed for the formation of fullerine structures including nanotubes.

It maybe desired to have certain materials within the nanotubes or balls in which case additional precursor materials can be fed in with the carbonaceous precursors to form the fullerine. Therefore, you may have a filled fullerine tube or ball with the end desired materials. These fullerenes may further be coated or whatever carbonation form is formed by this seeded stock may be further coated downstream with materials such as catalysts and encapsulation systems that may keep the materials separated such as polymers.

Current carbon plants are large volume with significant shipping costs and distances. By using a small flame based system, the amount needed and required in different applications can be made locally, can be varied locally on a Just-in-Time manufacturing basis for specific customers. So rather than another part or separate invention, a new business model can be patented now. Wherein the current carbon black, carbonaceous material industry sector depends on central manufacture at large facilities of the material which is then distributed. Logistically this is difficult due to the extremely low density of the soots that requires high shipping volumes on a product that is sold at a low price/pound, resulting in high shipping charges per product cost.

By making a modular, smaller volume system that is made many times, you enable the low capital structure systems that can be installed on a more regional basis and even at specific customer sites for the formation of the desired materials. Whether it be just plain carbon soots or carbon blacks or the enhanced size and shape un-agglomerated carbons or even the multi-carbon or carbonaceous forms discussed in the disclosure earlier. Therefore, this business model invention creates a new economic advantage over the current system of the carbon industry.

By use of the present invention pure carbon forms, seeded carbon forms, doped carbon forms, carbonaceous materials containing a wide range of matters can be formed and the materials can be zoned from seed to interdispersed to exterior coated completely or in-part with various



0175-PR

materials. Forming a broad range of carbons, carbonaceous materials with a wide range of potential applications from fillers, inks, dyes, stabilizers, catalysts, supports, and even further feed stocks for additional reactions that yield additional materials.

5 It could be that by forming materials in this way, carbides could be formed by further reaction — silicon carbide, nickel carbides, tungsten carbides, boron carbides — could all be formed from the primary carbon mixed extremely well with the carbon form. By bringing these primary materials to high temperature reactions, a more homogenous and pure forms of carbides are made.

10 The materials formed could also be used for chemical reactors and pyrotechnics as visually emissive elements inside the formed soots would be effective in yielding different colors for fireworks or other desired special effects.